

Status Report

**PHYSICAL PROPERTIES OF THE BIOPOLYMER CURDLAN
AND THE POTENTIAL APPLICATION AS A GELLED POLYMER
FOR PROFILE MODIFICATION**

Project BE5B, FY94

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ABSTRACT

For FY94, a biopolymer called curdlan was investigated as a potential agent for profile modification and plugging of high-permeability zones. Several attractive properties of this biopolymer warranted investigation as an agent for profile modification of CO₂ floods. Curdlan was soluble only in alkaline solutions. A firm gel was produced when the solution was acidified by reaction with CO₂. Alkaline solutions have a low viscosity when compared with other water soluble polymers. For polymer concentrations up to 1%, curdlan viscosities were less than 10 cP when measured at 23° C. Lower concentrations of NaOH, less than 0.22 M, produced significantly higher viscosity solutions. Polymer concentrations of 0.25% were sufficient to form a firm gel.

The results of gelation tests and viscosity measurements indicated that the polymer degraded with time in highly alkaline NaOH solutions. Polymer degradation was accelerated at higher temperatures. The rate of polymer degradation in NaOH solutions would not be acceptable for reservoir applications, especially for higher temperature reservoirs. To reduce polymer degradation, other chemicals with weaker basicity constants were studied. It was demonstrated that weaker bases including propyl amine, and mixtures of NH₄OH and Na₂CO₃ were sufficiently alkaline to hydrolyze and form acceptably low viscosity solutions. Viscosity measurements and gelation tests indicated a lower rate of polymer degradation with the weaker bases. However, polymer degradation does not appear to be acceptable at higher temperatures.

BACKGROUND

This project is directed to the development of methods to improve oil recovery for CO₂ flooding. Of the enhanced oil recovery (EOR) methods, gas-driven processes produce nearly one-third of the current EOR production. One of the problems associated with CO₂ floods is the occurrence of early CO₂ breakthrough which results in poor volumetric sweep efficiency. Because of gas channeling, portions of the reservoir are not contacted and displaced by the gas flood which results in bypassed oil. To recover unswept oil, a technique is required to restrict or block the higher permeability channels and direct injected CO₂ into less permeable reservoir areas which normally contain significant quantities of oil.

CURDLAN PRODUCTION

Presently, total curdlan production is small because of limited applications which include gel filtration and affinity chromatography, support for enzyme immobilization, research in food gelation, and research in anti-tumor properties. Curdlan is the general name for a series of closely related β glucan polymers composed mainly of 1,3- β -linkages. Curdlan (polymer 13140) used in this study was developed by the Japanese investigator T. Harada¹ at the Institute of Scientific and Industrial Research, Osaka University. He discovered a mutant strain of the microorganism *Alcaligenes faecalis* var. *myxogenes* that produced high curdlan yields from sugars when cultured at an appropriate pH. Curdlan is manufactured on a pilot plant scale by Wako Pure Chemicals, Ltd., Osaka, Japan. Another biopolymer with similar properties has been produced and patented by the University of Kansas. The biopolymer is produced by the *Cellulomonas flavigena* Strain KU.²

PHASE BEHAVIOR STUDIES

Experimental Procedure

Curdlan is a water insoluble polysaccharide which can be dissolved in alkaline solutions, and the polymer is insoluble in most organic solvents. A physical property study of the polymer curdlan was conducted to determine the rheological properties and solution viscosities, conditions for producing polymer gels, and the polymer stability at highly alkaline conditions. Curdlan, in a powder form, was obtained from Wako Pure Chemicals USA, Inc., and aqueous solutions were prepared on a weight basis where the polymer powder was considered to be 100% active. Other chemicals, such as NaOH, NH_4OH , and Na_2CO_3 used in this study, were research grade. The water was purified with a Millipore Water Purification System. Alkaline solutions with polymer were prepared in Erlenmeyer flasks by mixing at room temperature with a magnetic stirrer. After adding the compounds to the flask, the vapor space was purged with pure nitrogen and tightly sealed to minimize contact with air. Exclusion of the ambient air was necessary because CO_2 present in the air could react with and change the solution alkalinity. Viscosity measurements were made with either a Brookfield LVT or a Contraves viscometer.

Many polymer solutions are shear-thinning; therefore, apparent viscosities are a function of the shear-rate. A range of curdlan concentrations from 0.25 to 1% in solutions of 0.01 to 1 molar NaOH were measured to determine what effect solution pH and polymer concentration would have on viscoelastic properties. A Contraves viscometer was used for viscosity measurements because of the instrument's wide shear-rate capability. As shown by the examples in Fig. 1, the polymer solutions exhibited essentially Newtonian behavior. Therefore, for the purposes of these studies, the viscoelastic properties of these solutions could be adequately

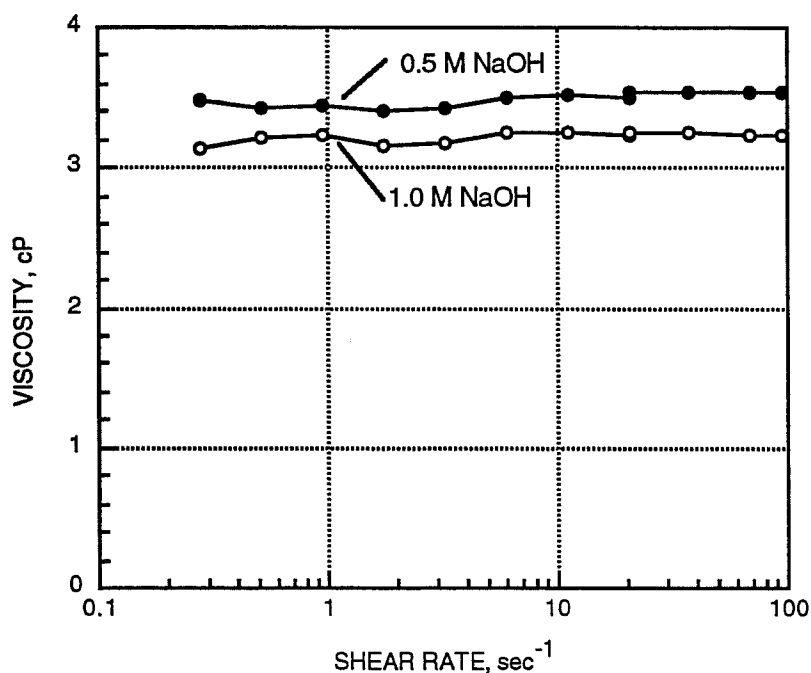


FIGURE 1. - Viscosity versus shear-rate for 0.5% curdlan in NaOH solution after solution aging for 2 weeks at 23°C.

described by a viscosity measurement at a single shear-rate. A Brookfield LTV viscometer was used for all other viscosity measurements at the instrument's optimum shear-rate.

Some pH measurements were made with an Orion digital pH meter model 611. The solutions required for the polymer hydrolysis were highly basic, in the range of pH 9.5 or greater. In this range, it was found that the pH measurements were not sufficiently accurate to provide meaningful pH values; therefore, all alkaline solutions were prepared and reported as molar concentrations.

Phase and Physical Property Studies of Curdlan Solutions

Curdlan was virtually insoluble in water at room temperature. Curdlan has some unusual thermal properties. According to Harada,¹ when an aqueous curdlan suspension was heated, a thermally stable gel was formed at about 60° C, with the gel viscosity increasing rapidly upon cooling. Also, the gel strength remained almost constant between a temperature of 60° and 80° C. At higher gel temperatures, 80° to 100° C, the gel strength increased by a factor of over two.

Only at elevated temperatures would the polymer partially hydrolyze to form a gel. In sufficiently alkaline solutions, the polymer hydrolyzed to form a clear viscous liquid. Although the polymer was soluble in 0.005 M NaOH, over time the solution would increase in viscosity and

form a gel, probably due to NaOH reaction with ambient CO₂ present in the solution and atmospheric air. These studies were limited to a more practical lower limit of 0.01 molar NaOH.

Figure 2 shows the change in solution viscosities with 0.25, 0.5, and 1% polymer concentrations in 1 M NaOH. A polymer concentration of 0.25% in NaOH solutions formed a weak gel when acidified with CO₂ or HCl. At this concentration, a highly deformable but nonflowing gel, was produced indicating an approximate lower limit for producing a gel. For the solutions of 0.5 and 1 M NaOH, the increase in viscosity was approximately proportional to the polymer concentration.

Of interest in this project was the relatively low viscosity of the polymer in sufficiently alkaline conditions. However, as shown in Fig. 2 for the 1% polymer solution, there was nearly a 5-fold increase in viscosity between the 0.1 and 0.5 M NaOH. The reason for the viscosity increase was studied previously by other investigators. Ogawa, et al.³ used optical rotary dispersion, viscosity, and flow birefringence to show a change in molecular conformation in the range of 0.19 to 0.24 M NaOH. They suggested that at lower NaOH concentrations the polymer takes an ordered conformation as a helix, whereas at higher NaOH concentrations, the polymer behaves as a random coil. Saito, et al.⁴ substantiated the helix-coil transition proposed by Ogawa using ¹³C NMR. In dilute alkaline solutions up to 0.19 M NaOH, the NMR spectra were essentially the same as that of a rigid gel. For 0.22 M and higher NaOH concentrations, the ¹³C signals decreased to less than one-tenth of the helix signal, a characteristic of a helix-to-coil transition. At lower alkaline conditions, increased solution viscosity was an indication of an ordered conformation. To obtain the advantage of low polymer viscosity, these studies indicated highly alkaline solutions would be required, i.e., solutions with a concentration greater than 0.22 M NaOH.

Polymer Stability and Gelation Studies with NaOH Solutions

A series of polymer solutions were prepared in different molar concentrations of NaOH. Figures 3 and 4 show the polymer solution viscosities measured at 23° C for 0.5% and 1% curdlan in 0.01 to 1 molar NaOH solutions. The solutions maintained at room temperature were measured for viscosity at periodic intervals. The solutions decreased in viscosity as the solutions aged for a wide range of NaOH concentrations.

Other viscosity measurements were made for solutions aged at 50° C, which are shown in Fig. 5. All viscosities measurements were at the same temperature of 23° C. Comparison of Figs. 4 and 5 shows an accelerated decrease in viscosity for the solutions aged at 50° C. Reaction of NaOH with the polymer was believed to be responsible for the decrease in solution viscosity. The rate of polymer reaction with NaOH increased at the higher temperature resulting in faster

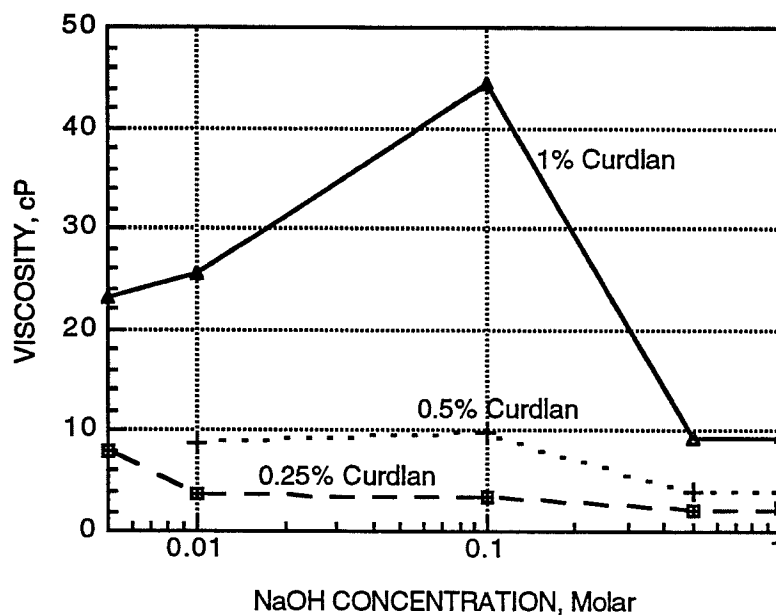


FIGURE 2. - Viscosities of 0.25, 0.5, and 1% curdlan in NaOH solutions ranging from 0.005 to 1 M.

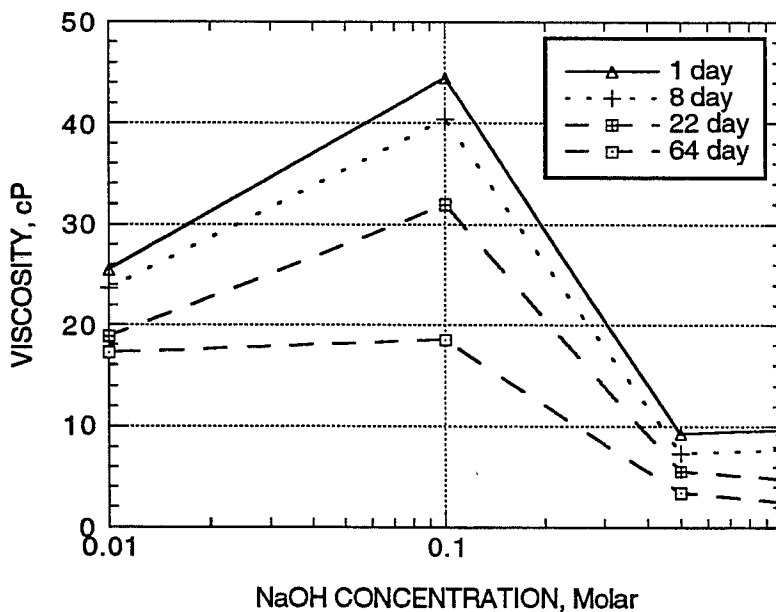


FIGURE 3. - Viscosities of 1% curdlan in solutions ranging from 0.01 to 1 molar NaOH after aging at 23° C.

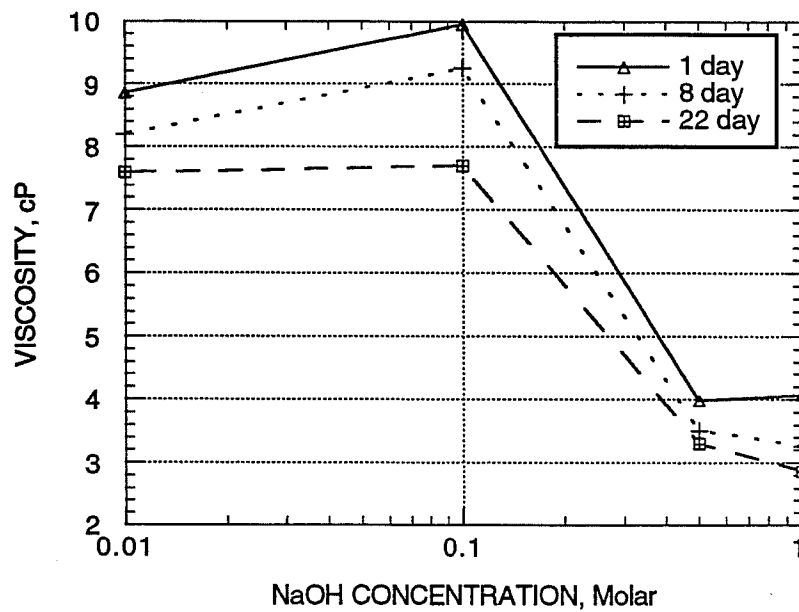


FIGURE 4. - Viscosities of 0.5% curdlan in solutions ranging from 0.01 to 1 molar NaOH after aging at 23°C.

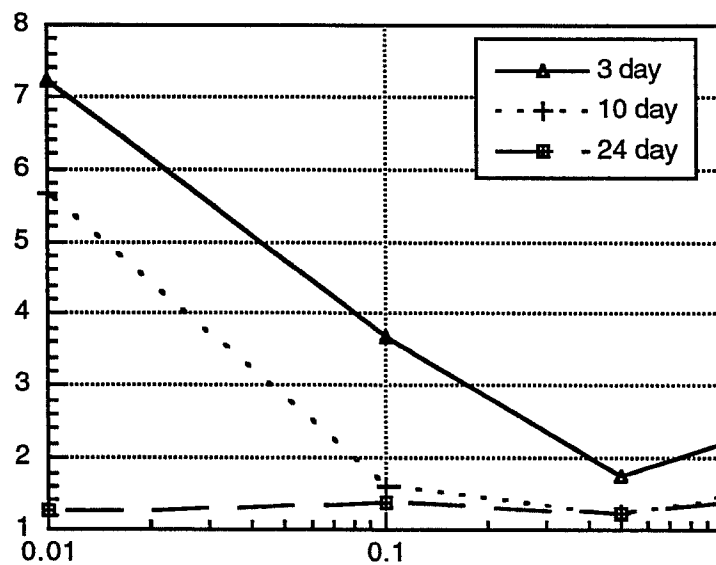


FIGURE 5. - Viscosities of 0.5% curdlan in NaOH solutions after aging at 50°C for 3, 10, and 24 days.

reaction and polymer degradation. Also, at 50° C, the relative change in viscosity was less for the solutions with lower NaOH concentrations. This suggests that the lower NaOH concentrations were less reactive and, therefore, reduced the rate of polymer degradation.

Gel Properties of NaOH Solutions

Periodic gelation tests were performed by neutralizing with small portions of the polymer solutions with HCl acid. The quality or gel strength was then observed according to the description listed in Table 1. Table 2 shows the gelation results of polymer solutions aged at room temperature. For the 1% curdlan solutions, a firm gel was obtained after a period of 11 weeks. However, a decrease in gel quality was observed after 8 to 10 weeks for the lower concentration curdlan solutions. There was also an indication that the solutions with higher NaOH concentrations produced lower quality gels.

Physical Properties of Other Alkaline Polymer Solutions

Since the curdlan polymer appeared to degrade in highly alkaline NaOH solutions, additional studies were made to investigate what effect weaker bases would have on polymer solubility and the potential for less polymer degradation. Solutions of 1% curdlan were prepared in NH₄OH.

TABLE 1. - Physical description of gel strength for alkaline curdlan solution after neutralization.

Gel Strength Code	Description of Gel Strength
A	No gel formed. The gel appears same viscosity as the original polymer solution.
B	Highly flowing gel. The gel appears to be only slightly more viscous than the initial polymer solution.
C	Flowing gel. Detectable gel with the gel rapidly flowing to the bottle cap upon inversion.
D	Moderately flowing gel. Gel slowly flows to the bottle cap upon inversion.
E	Barely flowing gel. Gel does not readily flow to the bottle cap upon inversion.
F	Highly deformable nonflowing gel. Gel readily deforms but does not flow upon inversion.
G	Slightly deformable nonflowing gel. Gel surface slightly deforms upon inversion.
H	Rigid gel. No gel surface deformation upon inversion with gel syneresis.

TABLE 2. - Description of curdlan gels which were aged at room temperature.

Curdlan Concentration, %	NaOH Concentration, Molar	Time of Solution Aging at 23° C, weeks					
		2	4	6	8	10	11
1	1	H	H	H	H	H	H
	0.5	H	H	H	H	H	H
	0.1	H	H	H	H	H	H
	0.10	H	H	H	H	H	H
0.5	1	G	G	G	G	D	
	0.5	G	G	G	G	F	
	0.1	G	G	G	G	G	
	0.10	G	G	G	G	G	
0.25	1	F	F	E	D		
	0.5	F	F	F	D		
	0.1	F	F	F	D		
	0.10	F	F	F	E		

Curdlan hydrolyzed in 0.1 and 1.0 M NH_4OH solutions, but formed cloudy gels. The solutions were sufficiently high in pH to hydrolyze or dissolve the polymer but too low to prevent gelation. The alkalinity of NH_4OH solution appeared to be near the transition point required for polymer gelation. The basicity constant of NH_4OH at 25°C is 1.8×10^{-5} , and a stronger base is required to prevent gelation.

To increase the solution alkalinity, other polymer solutions were prepared by combining mixtures of NH_4OH with Na_2CO_3 . For the series of solutions, the combined molarity of the two bases was maintained at 1 M. Figure 6 shows the viscosities of 0.5% curdlan in these mixtures at 23°C . The solutions were stirred for 1 day at room temperature prior to viscosity measurement. As stated previously, the solution with 1 M NH_4OH formed a gel. The solutions were sufficiently basic to form a clear solution between 0.1 to 0.75 M Na_2CO_3 (with 0.9 to 0.25 M NH_4OH). The viscosity reached a minimum of about 6 cP for the solution with equal molar concentrations (0.5 M) of NH_4OH and Na_2CO_3 . A higher molar concentration of NH_4OH and Na_2CO_3 yielded only a modest decrease in solution viscosity. The viscosity of a solution with twice the concentration (1 M Na_2CO_3 and 1 M NH_4OH) measured 5.2 cP.

Gelation tests were made with 0.5% polymer in solutions of Na_2CO_3 and NH_4OH . Base concentrations are listed in Table 3. Initially, the solutions formed gels with a gel strength of G.

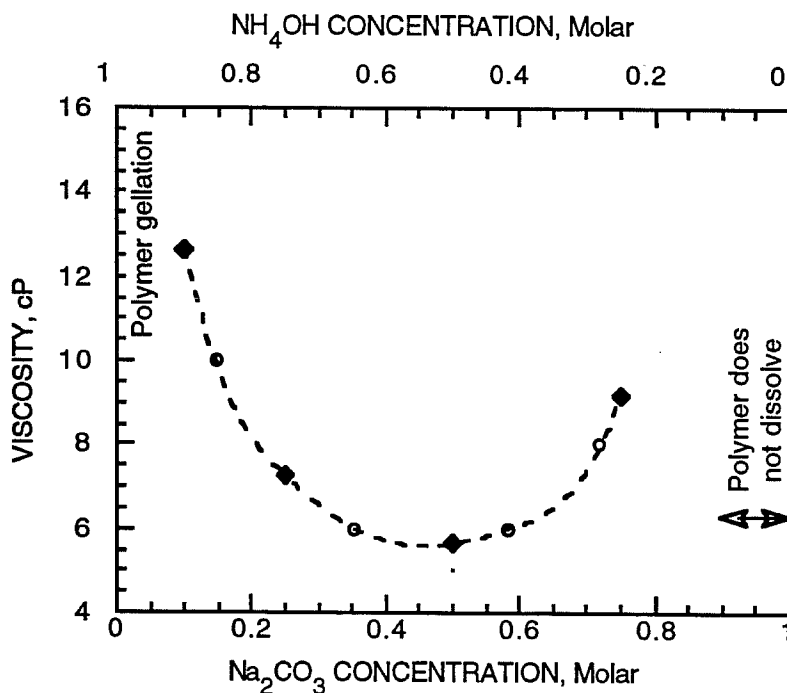


FIGURE 6. - Viscosities of 0.5% curdlan in NH_4OH and Na_2CO_3 solutions at 23°C .

After aging the solutions at 50° C for 30 days, there was a noticeable decrease in gel quality obtained after neutralization, as shown in Table 3. Gels produced after neutralization were low quality. Virtually no gel was formed with the 0.5 M Na₂CO₃ and 0.5 M NH₄OH solution. This was also the base concentration which produced the lowest solution viscosity, as shown in Fig. 6. Again the gelation tests indicated polymer degradation, although the rate of degradation was slower than that for solutions with NaOH.

Other polymer mixtures were prepared with Na₂B₂O₄ and NH₄OH. Again, the combined molarity of the two bases was maintained at 1 M. Because of higher molecular weight, a greater weight of Na₂B₂O₄ was required to obtain the same molar concentration as compared to Na₂CO₃. For a 0.5 M NH₄OH solution, a 0.5 M concentration of Na₂B₂O₄ was not completely soluble. Therefore, only a lower concentration of 0.25 M Na₂B₂O₄ was prepared with 1% curdlan and 0.75 M NH₄OH. This mixture had a viscosity of 7.9 cP. The tests indicated Na₂B₂O₄ with NH₄OH could be used to hydrolyze and produce a reasonably low viscosity polymer solution.

Aliphatic primary amines are somewhat stronger bases than ammonia. Propyl amine has a basicity constant of 4.7×10^{-4} . Because of the higher basicity constant, colorless solutions were made with the curdlan polymer in propyl amine concentrations of 0.1, 0.5, and 1 M. As shown in Fig. 7, only a small change in solution viscosities (less than 2 cP) was measured for the different amine concentrations with 0.5% polymer. After aging the samples for 4 days at 50° C, there was a measurable decrease in solution viscosities. The decrease in viscosity indicated there was some polymer degradation with the weaker base, although the degradation rate was less than that with NaOH.

Each of the polymer and propyl amine solutions was neutralized with HCl. Initially, gels were produced with a gel strength of G to H. Also, gels formed with HCl had a similar gel strength after the polymer solution was aged for 10 days at 50° C. As mentioned previously, for

TABLE 3. - Gel strength gels formed by neutralization after aging the 0.5% solutions for 30 days at 50° C.

Base Concentration	Gel Strength	
	after 2 hours	after 24 hours
0.1 M Na ₂ CO ₃ + 0.9 M NH ₄ OH	E	D
0.25 M Na ₂ CO ₃ + 0.75 M NH ₄ OH	C	B
0.5 M Na ₂ CO ₃ + 0.5 M NH ₄ OH	B	B
0.9 M Na ₂ CO ₃ + 0.1 M NH ₄ OH	D	E

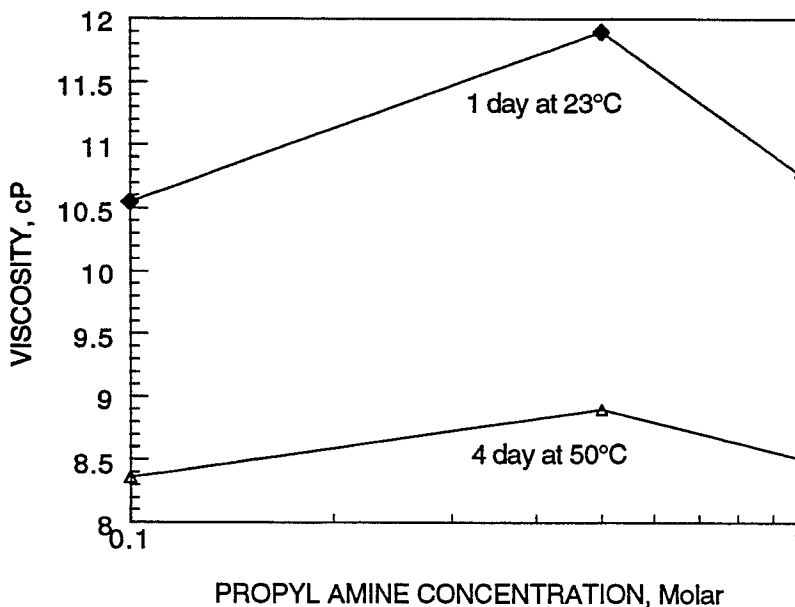


FIGURE 7. - Viscosities of 0.5% curdlan in propyl amine solutions measured at 23° C. The viscosities decreased by about 2 cP after aging for 4 days at 50° C.

NaOH solutions aged for this time period at 50° C, no gels were formed upon neutralization. This indicates the polymer was more stable in the amine solutions. Tests are continuing to determine if the polymer is more stable at these conditions over extended time intervals.

Effect of Formaldehyde

The previous experiments indicated polymer degradation at highly alkaline conditions. Bacterial degradation was possibly responsible. Therefore, other polymer solutions were made with formaldehyde (650 ppm) as a biocide in NaOH solutions. However, after heating the solutions at 50° C, there was no improvement in the rate of polymer degradation. No gels were obtained after aging for 1 week. This indicated that bacterial activity was not responsible for polymer degradation.

The addition of formaldehyde, however, appeared to change some of the polymer solution properties. The viscosities of 1% curdlan in NaOH with 650 ppm formaldehyde are shown in Fig. 8. The initial viscosities peaked at about 48 cP for 0.01 M NaOH. Comparison of similar solutions without formaldehyde (Fig. 3) shows a maximum viscosity (about 44 cP) for the 0.1 M NaOH solution.

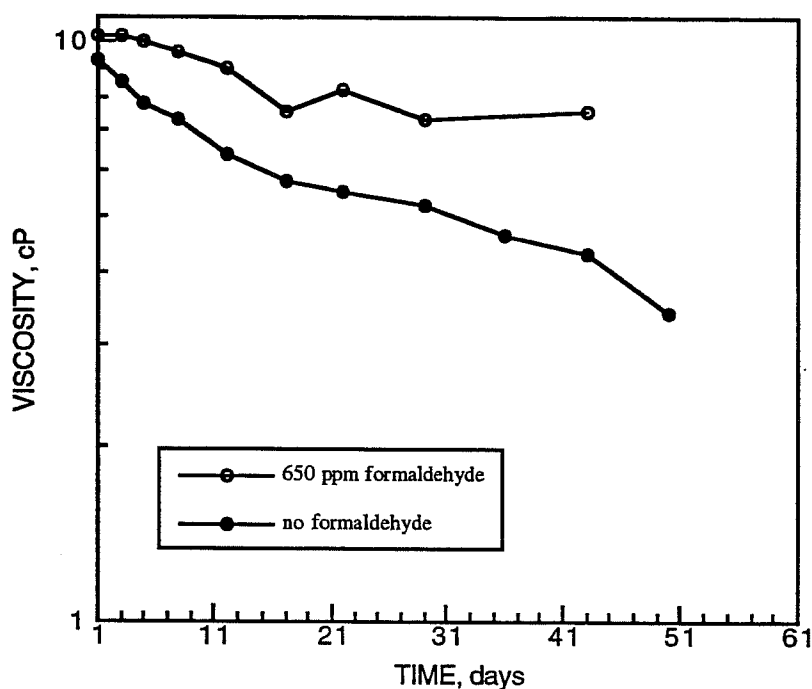


FIGURE 8. - Viscosities of 1.0% curdlan in 0.5 M NaOH solutions with and without 650 ppm formaldehyde aged at 23° C.

There was further evidence of formaldehyde activity in the curdlan solutions. Figure 8 shows the decline with time of viscosities with and without formaldehyde in 0.5 M NaOH. The decline in viscosity was less for the solutions containing formaldehyde. This may indicate that formaldehyde had a stabilizing effect on polymer degradation. However, it was also found after 60 days of aging, the solutions with formaldehyde started to increase in viscosity and the solutions became shear sensitive. This may indicate that formaldehyde was interacting with the polymer causing some mechanism, such as crosslinking, to increase the solution viscosity. At present, the exact mechanism for these viscosity changes is not known. It may be possible, however, to use some chemical additive which would stabilize the polymer and reduce polymer degradation.

CONCLUSIONS

1. This study showed that solutions of curdlan have relatively low viscosities in highly alkaline NaOH solutions. For polymer concentrations up to 1% curdlan in highly basic NaOH solutions, viscosities were less than 10 cP when measured at 23° C. Lower concentrations of NaOH (< 0.22 M) produced significantly higher viscosity solutions.

2. Gels were formed by neutralizing the solution with an acid. Gaseous CO₂ could be used to effectively neutralize the solutions. Gelation tests indicated that polymer concentrations of 0.25% are sufficient to form a firm gel.

3. The results of gelation tests and viscosity measurements indicated the polymer degraded with time in the highly alkaline NaOH solutions, and polymer degradation was accelerated at higher temperatures. The rate of polymer degradation in NaOH solutions are not acceptable for reservoir applications, especially for higher temperature reservoirs.

4. To reduce polymer degradation, other chemicals with weaker basicity constants were studied. It was demonstrated that weaker bases including propyl amine, and mixtures of NH₄OH and Na₂CO₃ are sufficiently alkaline to hydrolyze and form acceptably low viscosity solutions.

5. Viscosity measurements and gelation tests indicated a lower rate of polymer degradation with the weaker bases. However, polymer degradation does not appear to be acceptable at higher temperatures.

6. Polymer degradation, even at a lower rate using a weaker base, make mobility control applications less cost effective. Also, a weaker base, such as propyl amine, would increase the cost of mobility control applications when compared with the use of NaOH.

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